

# PATENT ABSTRACTS OF JAPAN

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## (54) ADHESIVE COMPOSITION FOR LAMINATING HAVING EXCELLENT RETORT RESISTANCE

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a two-part curing adhesive composition for laminating having excellent retort resistance.

SOLUTION: This two-part curing adhesive composition for laminating comprises a polyester-polyol obtained by reacting a polybasic acid with a polyhydric alcohol as a principal component and a polyisocyanate as a curing agent. In the two-part curing adhesive composition, the polybasic acid is characterized by comprising at least (1) a dimer acid containing  $\leq$ 10 mass% of a monomer acid component,  $\geq$ 70 mass% of a dimer acid component and  $\leq$ 20 mass% of a trimer acid component and (2) one or more kinds selected from othophthalic acid, terephthalic acid and isophthalic acid in an amount of 1.5-3.0 mmol/g based on the polyester-polyol.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention]This invention relates to the adhesive composition for 2 liquid hardening type lamination which is excellent in retort tolerance. In detail, a various plastic film and metal deposition film, aluminium foil, etc. are laminated, and it is related with the adhesive composition for 2 liquid hardening type lamination used when manufacturing the complex film used mainly for the wrapping of foodstuffs.

**[0002]**

[Description of the Prior Art]A dry lamination is art laminated while carrying out evaporation dry removal of the solvent after applying adhesives to one material face and heating and sticking other materials by pressure. This art can paste arbitrary films together freely, and since it can obtain the complex film which has the performance according to the purpose, it is widely used for manufacture of the wrapping of the foodstuffs in which high performance is demanded.

[0003]The polyester polyol of the terminal hydroxyl groups obtained from polyol and dicarboxylic acid as typical base resin with which practical use is presented, Polyester polyol and the polyester polyurethane polyol obtained from organic diisocyanate, Polyether polyol and the polyether polyurethane polyol obtained from organic diisocyanate, The polyester polyether polyurethane polyol obtained from the mixture and organic diisocyanate of polyester polyol and polyether polyol is mentioned, and each of these is the polyols of two organic functions thru/or three organic functions.

[0004]The adduct produced as a hardening agent on the other hand by adding 3-mol organic diisocyanate to 1 mol of trimethylolpropane, The organic polyisocyanate of many organic functions which has connection forms, such as buret produced by making 1 mol of water react to 3-mol organic diisocyanate or isocyanurate obtained by the polymerization of 3-mol organic diisocyanate, is used. It is used as the polyurethane polyisocyanate Lord produced by making

low molecule polyol react to these by polyisocyanate, polyester polyol, polyether polyol, or necessity.

[0005]The equivalent ratio of a hydroxyl group/isocyanate group is mixed at a rate of 1 / 1 - 1/3, adds ethyl acetate as a diluting solvent, and above-mentioned base resin and hardening agent generally prepare the blend liquid of adhesives in many cases.

[0006]From the complex film manufactured by the aforementioned dry lamination, it heat seals, a pouch (foodstuffs wrapping material) is created, and it fills up with contents further.

Application-of-pressure heat sterilization treatment called after this retorting (115 \*\* - 135 \*\*) may be performed. Under the present circumstances, if the hot water resistance of adhesives is low, the delamination in which a complex film exfoliates will be caused. The composition in which especially this contains aluminum foil, for example, PET (polyethylene terephthalate film) / aluminum foil / CPP (non-stretched polypropylene film), In complex films, such as PET/Ny (nylon film) / aluminum foil / CPP, PET / aluminum foil / Ny/CPP, delamination may occur in change of the gestalt of a pouch, shape, and retort conditions.

[0007]In order to solve the above-mentioned problem, to JP,58-11912,B, it is indicated that the retort tolerance of adhesives improves by adding a silane coupling agent. In JP,61-4864,B, the art of aiming at improvement in retort tolerance by adding an epoxy resin to a silane coupling agent further is indicated. To JP,3-68916,B, it is indicated that retort tolerance improves using the polyester polyol to which anhydrous aromatic polyvalent carboxylic acid was made to react. However, the actual condition is that adhesives the adhesives currently indicated by these have the problem that flexibility is low since the composition raw material of polyol is expensive, although it has the above-mentioned retort tolerance, and compatible in retort tolerance and flexibility are not yet obtained.

[0008]

[Problem(s) to be Solved by the Invention]Using dimer acid as a composition raw material of polyester polyol, the technical problem of this invention has high flexibility, and there is in providing the adhesive composition for 2 liquid hardening type lamination which is excellent in retort tolerance.

[0009]

[Means for Solving the Problem]A result of having repeated research wholeheartedly in order that this invention persons might solve an aforementioned problem, An adhesive composition for 2 liquid hardening type lamination using polyester polyol produced by making polybasic acid and polyhydric alcohol containing the phthalic acid of a specific amount and specific dimer acid react reached having-effect excellent in retort tolerance title this invention.

[0010]Namely, this invention uses as base resin polyester polyol produced by reacting polyhydric alcohol to polybasic acid, It is an adhesive composition for 2 liquid hardening type lamination which uses polyisocyanate as a hardening agent, Dimer acid whose trimer acid

component of more than 70 mass % of the polybasic acid below 10 mass % and a dimer acid ingredient is [ (1) monomer acid component ] below 20 mass % at least, (2) Provide an adhesive composition for 2 liquid hardening type lamination which contains 1.5 - 3.0 millimol / g for one or more sorts chosen from alt.phthalic acid, terephthalic acid, and isophthalic acid to polyester polyol.

[0011]

[Embodiment of the Invention]The adhesive composition for 2 liquid hardening type lamination of this invention, Polyester polyol produced by reacting polyhydric alcohol to polybasic acid is used as base resin, They are the adhesives for 2 liquid hardening type lamination which use polyisocyanate as a hardening agent, The dimer acid whose trimer acid component of more than 70 mass % of the above mentioned polybasic acid below 10 mass % and a dimer acid ingredient is [ (1) monomer acid component ] below 20 mass % at least, (2) 1.5 - 3.0 millimol / g is included for one or more sorts chosen from alt.phthalic acid, terephthalic acid, and isophthalic acid to polyester polyol.

[0012](Dimer acid) The polybasic acid used in order to form the polyester polyol used for the adhesive composition for 2 liquid hardening type lamination of this invention contains dimer acid as an essential ingredient. Dimer acid is output of the Diels ARUDA type dimerization reaction of unsaturated fatty acid of C18, such as oleic acid and linolic acid, and there are various things, such as what adds and saturated hydrogen in the unsaturated bond. This dimer acid comprises a monomer acid component, a dimer acid ingredient, and a trimer acid component. This dimer acid is condensed with polyhydric alcohol as some polybasic acid, and polyester polyol is compounded. In a dimer acid ingredient, in this invention, a monomer acid component uses the dimer acid not less than 70% of weight and whose trimer acid component are 20 or less % of the weight at least 10 or less % of the weight. Preferably, in a monomer acid component, a dimer acid ingredient is [ not less than 80% of weight and a trimer acid component ] 15 or less % of the weight at least 5 or less % of the weight. If a monomer acid component exceeds 10%, it will be hard to go up the molecular weight of the polyester polyol to generate, and the problem whose point constructing a bridge decreases will occur. If a trimer acid component exceeds 20%, when compounding polyester polyol, the danger of presenting and gelling the three-dimensional structure occurs.

[0013]As dimer acid, the BASA dimes 216 and 228 and the em poles 1019, 1004, 1061, and 1062 (made by a cog varnish company) can be mentioned, for example.

[0014](phthalic acid) The polybasic acid used in order to form the polyester polyol used for the adhesive composition for 2 liquid hardening type lamination of this invention, One or more sorts of phthalic acid chosen from alt.phthalic acid, terephthalic acid, and isophthalic acid is included as 1.5 to 3.0 millimol /g, and an essential ingredient to 1 g of polyester polyol. If there is a tendency which is inferior to retort tolerance when 3.0 millimols / g is exceeded and it is

less than 1.5 millimols / g, the tendency of the fall of retort tolerance and the adhesive fall to aluminum foil will be seen.

[0015](Other polybasic acid) As polybasic acid used in order to form the polyester polyol used for the adhesive composition for 2 liquid hardening type lamination of this invention, besides above mentioned indispensable dimer acid and phthalic acid, if publicly known as polybasic acid, any raw material can be used together. For example, succinic acid, adipic acid, azelaic acid, sebacic acid, dodecane dicarboxylic acid, A maleic anhydride, fumaric acid, 1,3-cyclopentane dicarboxylic acid, 1, 4-cyclohexanedicarboxylic acid, 1, 4-naphthalene dicarboxylic acid, 2, 5-naphthalene dicarboxylic acid, 2, 6-naphthalene dicarboxylic acid, The anhydride or ester plasticity derivative of naphthalic acid, biphenyl dicarboxylic acid, 1,2-bis (phenoxy)ethane-p,p'-dicarboxylic acid, and these dicarboxylic acid; Para-hydroxybenzoic acid, it is independent about polybasic acid, such as an ester plasticity derivative of p-(2-hydroxyethoxy) benzoic acid and these dihydroxycarboxylic acid, -- it is -- it can be used with two or more sorts of mixtures.

[0016](Polyhydric alcohol) As polyhydric alcohol used in order to form the polyester polyol used for the adhesive composition for 2 liquid hardening type lamination of this invention, if it is publicly known and is, all can be used. As an example, ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pantanediol, 3-methyl-1,5-pantanediol, 1,6-hexanediol, neopentyl glycol, methyl pentanediol, Dimethylbutanediol, a butylethylpropanediol, a diethylene glycol, Triethylene glycol, tetraethylene glycol, dipropylene glycol, Tripropylene glycol, screw hydroxyethoxybenzene, 1,4-cyclohexanediol, 1,4-cyclohexane dimethanol, triethylene glycol, polycaprolactone diol, Glycols, such as dimer diol, bisphenol A, and hydrogenation bisphenol A. Propiolactone, a butyrolactone, epsilon-caprolactone, delta-valerolactone, The polyester obtained by the ring-opening-polymerization reaction of cyclic ester compounds, such as a beta-methyl-delta-valerolactone. Ethylene glycol, a diethylene glycol, triethylene glycol, propylene glycol, a trimethylene glycol, 1,3-butanediol, 1,4-butanediol, Use as an initiator one sort of the compound which has two active hydrogen atoms, such as 1,6-hexanediol and neopentyl glycol, or two sorts or more, and Ethyleneoxide, Propylene oxide, butylene oxide, styrene oxide, It is independent or polyhydric alcohol components, such as polyether which carried out addition condensation of one sort of monomers, such as epichlorohydrin, a tetrahydrofuran, and cyclohexylene, or the two sorts or more with the conventional method, can be used as two or more sorts of mixtures. Use of dimer diol is preferred at the point of excelling especially in retort tolerance also in these. Dimer diol is obtained by making the aforementioned dimer acid return. As dimer diol, Pes Paul HP-1000 (made by a cog varnish company) can be mentioned, for example.

[0017]The hydroxyl group concentration in the polyester polyol used for the adhesive composition for 2 liquid hardening type lamination of this invention is per said 1g of polyester

polyol, and 0.01 to 0.25 millimol, and the desirable adhesive strength to better retort tolerance and aluminum foil is obtained.

[0018]The polyester polyol used for the adhesive composition for 2 liquid hardening type lamination of this invention, In adhesion of the nylon/aluminum used abundantly as an wrapping material retorted, adhesion of PET/nylon, etc., improvement in adhesive strength is found by using the polyester polyurethane polyol which urethane-ized this polyester polyol. As organic diisocyanate used for urethane-ization, Diphenylmethane diisocyanate, xylylene diisocyanate, Tetramethyl xylylene diisocyanate, tolylene diisocyanate, Aromatic diisocyanate, such as a prepolymer with low molecule glycols and said aromatic diisocyanate, 1,6-hexamethylene diisocyanate, 2 and 2, 4-trimethyl hexamethylene di-isocyanate, Aliphatic series diisocyanate, such as a prepolymer with low molecule glycols, such as lysine diisocyanate, ethylene glycol, and propylene glycol, and said aliphatic series diisocyanate, Isophorone diisocyanate, the hydrogenation-izing 4, 4'-diphenylmethane diisocyanate, Alicycle fellows diisocyanate, such as a prepolymer with methyl cyclohexylene diisocyanate, isopropylidene dicyclohexyl 4,4'-diisocyanate, and low molecule glycols and said alicycle fellows diisocyanate, and two or more sorts of these mixtures are mentioned.

[0019]In the case of urethane-izing, aforementioned polyhydric alcohol and polyether polyol can be used in addition to the aforementioned polyester. Aforementioned polyhydric alcohol and polyether polyol ingredient can also be blended and used for these polyester and polyurethane.

[0020](Hardening agent) the polyisocyanate used as a hardening agent used for the adhesive composition for 2 liquid hardening type lamination of this invention can use the same thing as the polyisocyanates used as a hardening agent of the conventional 2 liquid reaction type polyurethane adhesive indicated by the paragraph of the Prior art. For example, the adduct object of the aforementioned organic diisocyanate and polyols, the isocyanurate object of the aforementioned organic diisocyanate, a view let object, and an allophanate object are mentioned.

[0021](Adhesion promoter) An adhesion promoter can also be used again in the adhesive composition for 2 liquid hardening type lamination of this invention. Coupling agents, such as a silane coupling agent, a titanate system coupling agent, and an aluminum system, an epoxy resin, etc. are mentioned to an adhesion promoter.

[0022]As a silane coupling agent, for example gamma-aminopropyl triethoxysilane, gamma-aminopropyl trimethoxysilane, N-beta (aminoethyl)-gamma-aminopropyl trimethoxysilane, N-beta (aminoethyl)-gamma-aminopropyl trimethyl dimethoxysilane, Aminosilanes, such as N-phenyl-gamma-aminopropyl trimethoxysilane; beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, Eoxysilane, such as gamma-glycidoxypropyltrimetoxysilane and gamma-glycidoxyl propyltriethoxysilane; Vinyltris (beta-methoxyethoxy) Silang, Vinylsilane,

such as vinyltriethoxysilane, vinyltrimetoxysilane, and gamma-methacryloxpropyl trimethoxy silane; hexamethyldisilazane, gamma-mercaptopropyltrimethoxysilane, etc. can be mentioned.

[0023]As a titanate system coupling agent, for example Tetraisopropoxy titanium, Tetra-n-butoxytitanium, a butyl titanate dimer, tetrastearyl titanate, titanium acetylacetone, titanium lactate, tetraoctylene glycol titanate, titanium lactate, tetra stearoxy titanium, etc. can be mentioned.

[0024]As an aluminate coupling agent, aceto alkoxy aluminum JIISOPUROPIRETO etc. can mention, for example.

[0025]The epi-bis type, novolac type which are generally marketed as an epoxy resin, beta-methyl EPIKURO type, an annular oxirane type, a glycidyl ether type, Various epoxy resins, such as a glycidyl ester type, a polyglycol ether type, a glycol ether type, an epoxidation fatty-acid-ester type, a polyvalent-carboxylic-acid ester type, an amino glycidyl type, and a resorcinol type, are mentioned.

[0026]In the adhesive composition for 2 liquid hardening type lamination of this invention, an acid anhydride publicly known as a method of raising the acid resistance of an adhesives layer can also be used together. As an acid anhydride, for example A phthalic acid anhydride, a succinic acid anhydride, a beef fat acid anhydride, Himic acid anhydride, a maleic acid anhydride, a tetrahydrophthalic anhydride, A hexa hydra phthalic acid anhydride, a tetra prom phthalic acid anhydride, a tetra KURORU phthalic acid anhydride, Trimellitic anhydride, a pyromellitic anhydride, a benzo FENO tetracarboxylic anhydride, 2,3,6,7-naphthalene tetracarboxylic acid 2 anhydride, the 5-(2,5-oxo tetrahydro furil)-3-methyl-3-cyclohexene 1, 2-dicarboxylic anhydride, a styrene maleic anhydride copolymer, etc. are mentioned.

[0027]The adhesive composition for 2 liquid hardening type lamination of this invention may be which gestalt of a solvent type or a solventless type. In a solvent type case, a solvent is used as a reaction medium at the time of manufacture of base resin and a hardening agent, and also is used as a diluent at the time of paint. As a solvent which can be used, for example, ester species, such as ethyl acetate, butyl acetate, and a cellosolve acetate, Ketone, such as acetone, methyl ethyl ketone, isobutyl ketone, and cyclohexanone. Halogenated hydrocarbon, such as aromatic hydrocarbon, such as ether, such as a tetrahydrofuran and dioxane, toluene, and xylene, methylenechloride, and ethylenechloride, dimethyl sulfoxide, dimethylsulfoamide, etc. are mentioned. It is preferred to usually use ethyl acetate among these.

[0028](A substrate and a complex film) As a substrate for complex films, a PET (biaxial-stretching polyethylene terephthalate) film, a nylon film, aluminum foil, a CPP (unextended polypropylene) film, etc. are used. The three-layer complex film of PET / aluminum foil / CPP, the four-layer complex film of PET / nylon / aluminum foil / CPP, etc. can be formed by carrying out spreading desiccation and laminating the adhesive composition for 2 liquid hardening type

lamination of this invention to these films. By using the adhesive composition for 2 liquid hardening type lamination of this invention, retort tolerance and adhesive strength excellent in the complex film which has especially an aluminum foil layer can be given.

[0029](Coating method) If the adhesive composition for 2 liquid hardening type lamination of this invention is publicly known, even if it will be applied with which coating method, it does not interfere, but it is generally applied with a gravure roll coating method. the coverage of these adhesives -- solid content -- 1.5 - 5 g/m<sup>2</sup> -- it is preferably used on the coating conditions of 2 - 4 g/m<sup>2</sup>.

[0030]

[Example]Although an example explains the contents and the effect of this invention still in detail below, this invention is not limited to the following examples. That it is the inside of an example "part" shows a "mass part."

[0031][The example 1 of preparation] In the polyester reaction container provided with a base resin A agitator, a thermometer, a nitrogen gas introducing pipe, a rectification tube, a water separator, etc. 9.4 copies of terephthalic acid, 37.8 copies of isophthalic acid, 17.9 copies of adipic acid, BASA dime 228 (cog varnish company, dimer fatty acid; acid value =196 mgKOH/g) 9.4 copy, 9.4 copies of ethylene glycol, 16.1 copies of neopentyl glycol, 15.1 copies of 1,6-hexanediol, and 0.03 copy of zinc acetate were prepared, it heated gradually and the internal temperature was held at 240 \*\* so that rectification tube top temperature might not exceed 100 \*\*. Xylene was added in the place where acid value became 5 mgKOH/g, reflux of the xylene was carried out at the temperature using the water separator, and the reaction was further continued to 2 or less mgKOH/g of acid value. It decompressed to 10 or less mmHg, and it held for 1.5 hours, xylene was removed, the esterification reaction was ended, and polyester polyol was obtained. This was diluted with ethyl acetate and the polyester polyol solution of Gardner viscosity T-U was obtained at 50% of nonvolatile matter o'clock. Let this be the base resin A.

[0032][The example 2 of preparation] In the polyester reaction container provided with a base resin B agitator, a thermometer, a nitrogen gas introducing pipe, a rectification tube, a water separator, etc. 41.2 copies of isophthalic acid, 22.8 copies of adipic acid, and the BASA dime 216 (a cog varnish company.) Dimer fatty acid; 9.8 copies of acid value =195 mgKOH/g, 9.9 copies of ethylene glycol, 18.4 copies of neopentyl glycol, 13.2 copies of 1,6-hexanediol, and 0.03 copy of zinc acetate were prepared, it heated gradually and the internal temperature was held at 240 \*\* so that rectification tube top temperature might not exceed 100 \*\*. Xylene was added in the place where acid value became 5 mgKOH/g, reflux of the xylene was carried out at the temperature using the water separator, and the reaction was further continued to 2 or less mgKOH/g of acid value. It decompressed to 10 or less mmHg, and it held for 1.5 hours, xylene was removed, the esterification reaction was ended, and intermediate polyester polyol

was obtained. Urethane-ization is reacted until it adds 4.7 copies of isophorone diisocyanate, it heats at 120 \*\* to 100 copies of obtained intermediate polyester polyol and the NCO group of isolation is lost substantially, It diluted with ethyl acetate and the polyester urethane polyol solution of Gardner viscosity V-W was obtained at 50% of nonvolatile matter o'clock. Let this be the base resin B.

[0033][The example 3 of preparation] In the polyester reaction container provided with a base resin C agitator, a thermometer, a nitrogen gas introducing pipe, a rectification tube, a water separator, etc. 27.3 copies of isophthalic acid, 33.4 copies of adipic acid, and the em pole 1062 (a cog varnish company.) Dimer fatty acid; 13.1 copies of acid value =196 mgKOH/g, 8.3 copies of ethylene glycol, 24.8 copies of neopentyl glycol, 8.2 copies of 1,6-hexanediol, and 0.03 copy of zinc acetate were prepared, it heated gradually and the internal temperature was held at 240 \*\* so that rectification tube top temperature might not exceed 100 \*\*. Xylene was added in the place where acid value became 5 mgKOH/g, reflux of the xylene was carried out at the temperature using the water separator, and the reaction was further continued to 2 or less mgKOH/g of acid value. It decompressed to 10 or less mmHg, and it held for 1.5 hours, xylene was removed, the esterification reaction was ended, and intermediate polyester polyol was obtained. As opposed to 100 copies of obtained intermediate polyester polyol, Urethane-ization was reacted, it diluted with ethyl acetate, and the polyester urethane polyol solution of the Gardner viscosity X was obtained at 50% of nonvolatile matter o'clock until it added 4.7 copies of isophorone diisocyanate, it heated at 120 \*\* and the NCO group of isolation was lost substantially. Let this be the base resin C.

[0034][The example 4 of preparation] In the polyester reaction container provided with a base resin D agitator, a thermometer, a nitrogen gas introducing pipe, a rectification tube, a water separator, etc. Terephthalic acid 23.8, 23.8 copies of isophthalic acid, 16.8 copies of adipic acid, Em pole 1062 (cog varnish company, dimer fatty acid; acid value =196 mgKOH/g) 9.3 copy, 9.5 copies of ethylene glycol, 17.5 copies of neopentyl glycol, 14.3 copies of 1,6-hexanediol, and 0.03 copy of zinc acetate were prepared, it heated gradually and the internal temperature was held at 240 \*\* so that rectification tube top temperature might not exceed 100 \*\*. Xylene was added in the place where acid value became 5 mgKOH/g, reflux of the xylene was carried out at the temperature using the water separator, and the reaction was further continued to 2 or less mgKOH/g of acid value. It decompressed to 10 or less mmHg, and it held for 1.5 hours, xylene was removed, the esterification reaction was ended, and intermediate polyester polyol was obtained. As opposed to 100 copies of obtained intermediate polyester polyol, Urethane-ization was reacted, it diluted with ethyl acetate, and the polyester urethane polyol solution of the Gardner viscosity U was obtained at 50% of nonvolatile matter o'clock until it added 2.6 copies of isophorone diisocyanate, it heated at 120 \*\* and the NCO group of isolation was lost substantially. Let this be the base resin D.

[0035][The example 5 of preparation] In the polyester reaction container provided with a base resin E agitator, a thermometer, a nitrogen gas introducing pipe, a rectification tube, a water separator, etc. 3.0 copies of terephthalic acid, 30.7 copies of isophthalic acid, 24.3 copies of adipic acid, BASA dime 228 (cog varnish company, dimer fatty acid; acid value =196 mgKOH/g) 11.9 copy, 5.5 copies of ethylene glycol, 24.8 copies of neopentyl glycol, 13.9 copies of 1,6-hexanediol, and 0.03 copy of zinc acetate were prepared, it heated gradually and the internal temperature was held at 240 \*\* so that rectification tube top temperature might not exceed 100 \*\*. Xylene was added in the place where acid value became 5 mgKOH/g, reflux of the xylene was carried out at the temperature using the water separator, and the reaction was further continued to 2 or less mgKOH/g of acid value. It decompressed to 10 or less mmHg, and it held for 1.5 hours, xylene was removed, the esterification reaction was ended, and intermediate polyester polyol was obtained. As opposed to 100 copies of obtained intermediate polyester polyol, Urethane-ization was reacted, it diluted with ethyl acetate, and the polyester urethane polyol solution of the Gardner viscosity P was obtained at 50% of nonvolatile matter o'clock until it added 8.5 copies of isophorone diisocyanate, it heated at 120 \*\* and the NCO group of isolation was lost substantially. Let this be the base resin E.

[0036][The example 1 of comparison preparation] In the polyester reaction container provided with a base resin F agitator, a thermometer, a nitrogen gas introducing pipe, a rectification tube, a water separator, etc. 4.8 copies of terephthalic acid, 33.6 copies of isophthalic acid, 23.3 copies of adipic acid, Em pole 1062 (cog varnish company, dimer fatty acid; acid value =196 mgKOH/g) 9.6 copy, Ant fat 47 (cog varnish company, dimer fatty acid; acid value =175 mgKOH/g) 1.1 copy, 5.3 copies of ethylene glycol, 23.8 copies of neopentyl glycol, 13.3 copies of 1,6-hexanediol, and 0.03 copy of zinc acetate were prepared, it heated gradually and the internal temperature was held at 240 \*\* so that rectification tube top temperature might not exceed 100 \*\*. Xylene was added in the place where acid value became 5 mgKOH/g, reflux of the xylene was carried out at the temperature using the water separator, and the reaction was further continued to 2 or less mgKOH/g of acid value. It decompressed to 10 or less mmHg, and it held for 1.5 hours, xylene was removed, the esterification reaction was ended, and polyester polyol was obtained. As opposed to 100 copies of obtained intermediate polyester polyol, Urethane-ization was reacted, it diluted with ethyl acetate, and the polyester urethane polyol solution of the Gardner viscosity M was obtained at 50% of nonvolatile matter o'clock until it added 2.6 copies of isophorone diisocyanate, it heated at 120 \*\* and the NCO group of isolation was lost substantially. Let this be the base resin F.

[0037][The example 2 of comparison preparation] In the polyester reaction container provided with a base resin G agitator, a thermometer, a nitrogen gas introducing pipe, a rectification tube, a water separator, etc. Terephthalic acid 4.6, 32.9 copies of isophthalic acid, 22.2 copies of adipic acid, Em pole 1062 (cog varnish company, dimer fatty acid; acid value =196

mgKOH/g) 9.1 copy, Em pole 1045 (cog varnish company, dimer fatty acid; acid value =190 mgKOH/g) 4.1 copy, 5.9 copies of ethylene glycol, 22.7 copies of neopentyl glycol, 12.7 copies of 1,6-hexanediol, and 0.03 copy of zinc acetate were prepared, it heated gradually and the internal temperature was held at 240 \*\* so that rectification tube top temperature might not exceed 100 \*\*. Xylene was added in the place where acid value became 5 mgKOH/g, reflux of the xylene was carried out at the temperature using the water separator, and the reaction was further continued to 2 or less mgKOH/g of acid value. It decompressed to 10 or less mmHg, and it held for 1.5 hours, xylene was removed, the esterification reaction was ended, and intermediate polyester polyol was obtained. When urethane-ization was reacted until it added 3.7 copies of isophorone diisocyanate, it heated at 120 \*\* to 100 copies of obtained intermediate polyester polyol and the NCO group of isolation was lost substantially, the solution thickened and it gelled after that.

[0038][The example 3 of comparison preparation] In the polyester reaction container provided with a base resin H agitator, a thermometer, a nitrogen gas introducing pipe, a rectification tube, a water separator, etc. Terephthalic acid 16.8, 37.7 copies of isophthalic acid, 10.1 copies of adipic acid, BASA dime 228 (cog varnish company, dimer fatty acid; acid value =196 mgKOH/g) 8.4 copy, 8.4 copies of ethylene glycol, 21.0 copies of neopentyl glycol, 12.6 copies of 1,6-hexanediol, and 0.03 copy of zinc acetate were prepared, it heated gradually and the internal temperature was held at 240 \*\* so that rectification tube top temperature might not exceed 100 \*\*. Xylene was added in the place where acid value became 5 mgKOH/g, reflux of the xylene was carried out at the temperature using the water separator, and the reaction was further continued to 2 or less mgKOH/g of acid value. It decompressed to 10 or less mmHg, and it held for 1.5 hours, xylene was removed, the esterification reaction was ended, and intermediate polyester polyol was obtained. As opposed to 100 copies of obtained intermediate polyester polyol, Urethane-ization was reacted, it diluted with ethyl acetate, and the polyester urethane polyol solution of Gardner viscosity Y-Z was obtained at 50% of nonvolatile matter o'clock until it added 4.3 copies of isophorone diisocyanate, it heated at 120 \*\* and the NCO group of isolation was lost substantially. Let this be the base resin H.

[0039]The mass ratio (%) and acid value (mgKOH/g) of each ingredient in the used dimer acid are described in the following table 1, and the contents of the above-mentioned base resin are described in Table 2 and 3.

[0040]

[Table 1]

商品名	モノマー酸 成分	ダイマー酸 成分	トリマー酸 成分	酸価 mgKOH/g
バーサダイム 2 16	8	7.7	1.5	19.5
バーサダイム 2 28	5	8.0	1.5	19.6
エムポール 1019	6	7.9	1.5	18.9
エムポール 1062	5	9.4	1	19.6
エムポール 1045	1	1.8	8.1	19.0
アリファット4 7	10.0	0	0	17.5

[0041]

[Table 2]

	主剤A	主剤B	主剤C	主剤D
モノマー酸成分%	5	8	5	5
ダイマー酸成分%	8.0	7.7	9.4	9.4
トリマー酸成分%	1.5	1.5	1	1
フタル酸類濃度 (ミリモル/g)	2.9	2.5	1.6	2.9
水酸基濃度 (ミリ当量/g)	0.22	0.12	0.08	0.25
ガードナー粘度	T-U	V-W	X	U

[0042]

[Table 3]

	主剤E	主剤F	主剤G	主剤H
モノマー酸成分%	5	1.4	4	5
ダイマー酸成分%	8.0	8.5	7.1	8.0
トリマー酸成分%	1.5	1	2.5	1.5
フタル酸類濃度 (ミリモル/g)	2.0	2.3	2.3	3.4
水酸基濃度 (ミリ当量/g)	0.30	0.10	—	0.24
ガードナー粘度	P	M	ゲル化	Y-Z

[0043][The example 1 of hardening agent adjustment] Let polyisocyanate of a hardening agent aKW-75 (made by Dainippon Ink & Chemicals, Inc.), and TDI (tolylene diisocyanate) system be the hardening agent a. It blended so that above-mentioned base resin and hardening agent might be described in the following Table 4 and 5, and the complex film was created using the adhesives, and evaluation of adhesive strength and retort tolerance was performed by the method shown below.

[0044]The manufacturing method of a complex film is shown below. The adhesives blend liquid which blended the ethyl acetate which is base resin, a hardening agent, and a diluting solvent as shown in Tables 4 and 5, Using a test laminating machine (product made from Musashino Machinery), it applies to a PET (biaxial-stretching polyethylene terephthalate) film so that it may become 3.5g (solid content) of coverage / m<sup>2</sup>, It laminated with the adhesive coated surface of PET and ONy (nylon film which carried out biaxial extension) to which the diluting solvent was volatilized with the dryer set as the temperature of 70 \*\*, it dried, and adhesives were applied, and the complex film which consists of two-layer [ of PET/ONy ] was created. To the ONy side of the complex film which laminated this PET and ONy, the adhesives concerned were applied and it dried so that it might become 3.5g (solid content) of coverage / m<sup>2</sup>, and this and aluminum foil (O material) were laminated, and the complex film which consists of three layers of PET/ONy/aluminum foil was created. To the aluminum foil side of the complex film of three layers which laminated this PET, ONy, and aluminum foil. The adhesives concerned were applied and it dried so that it might become 3.5g (solid content) of coverage / m<sup>2</sup>, and this and a CPP (unextended polypropylene) film were laminated, and the complex film which consists of four layers of PET/ONy / aluminum foil / CPP was created. Subsequently, EJINNGU for 50 \*\* x four days was performed for this complex film, adhesives were hardened, and the complex film of four layers was obtained.

[0045]The film used the following.

PET film : Toyobo Co., Ltd. make E-5100 12micromONy film : Unitika, Ltd. make Emblem  
 ONBC-RT 15micrometer aluminum foil : Product made from Toyo Aluminium Industry  
 ARUMIHAKU C 9micromCPP film : Toyobo Co., Ltd. make ZK-93K 70micrometer[0046]The valuation method of adhesives was shown below.

- (1) Tensile strength at the time of setting ambient temperature as 25 \*\*, setting exfoliation speed as a part for 300-mm/using a tension tester, and exfoliating between the aluminum foil of the complex film of a sample and CPP(s) which ended adhesive strength aging with T type peeling method was made into adhesive strength, and it was shown in Table 4 and 5. The unit of adhesive strength was set to N/15mm.
- (2) The pouch with a size of 120 mm x 120 mm was created using the complex film of the sample which retort tolerance aging ended. Under the present circumstances, heat sealing was performed on 200 \*\*, 98kPa, and the seal conditions for 1 second using the bar seal of 10-mm width. Subsequently, two folds were put into the flow direction (MD) and the transverse direction (TD), and the pouch was filled up with the false foodstuffs 70g which blended vinegar, vegetable oil, and meat sauce with 1:1:1 by the weight ratio as contents. After carrying out retort sterilization processing of the steamy type for 30 minutes for this pouch at 135 \*\*, viewing estimated delamination (float) for the appearance of the pouch.

[0047]

[Table 4]

	実施例 1	実施例 2	実施例 3	実施例 4
主剤A	1 0 0	—	—	—
主剤B	—	1 0 0	—	—
主剤C	—	—	1 0 0	—
主剤D	—	—	—	1 0 0
硬化剤 a	1 0	8	8	1 0
酢酸エチル	1 2 0	1 1 6	1 1 6	1 2 0
接着強度 (N/15mm)	1 4. 3	1 4. 2	1 2. 8	1 3. 5
レトルト耐性	浮き無し	浮き無し	浮き無し	浮き無し

[0048]

[Table 5]

	実施例 5	比較例 1	比較例 2
主剤E	1 0 0	—	—
主剤F	—	1 0 0	—
主剤H	—	—	1 0 0
硬化剤 a	1 2	8	1 0
酢酸エチル	1 2 4	1 1 6	1 2 0
接着強度 (N／15 mm)	9. 5	4. 5	1 5. 2
レトルト耐性	浮き無し	浮き有り	浮き有り

[0049]

[Effect of the Invention] This invention can provide the adhesive composition for 2 liquid hardening type lamination excellent in the retort tolerance which controls the delamination and bag tearing at the time of heating-at-high-temperature germicidal treatment.

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[Translation done.]